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硕 士 学 位 论 文

POSS 基共聚物的溶液自组装及其多重刺激响应研究

Study on Self-Assembly Behavior and Mutiple Stimuli-Responsive Property of POSS-Based Copolymers in Solution

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摘 要

有机-无机纳米复合材料因其同时具有有机聚合物和无机材料的优异性能，近年来引起了广泛的研究兴趣。天然的纳米尺度、规整的空间结构、易于设计的分子结构以及良好的溶解性的 POSS 的出现为有机/无机纳米杂化材料应用和发展提供了一种崭新的途径，为真正意义上的单纳米尺度和分子水平改性高分子提供了可能。然而，涉及 POSS 基聚合物溶液自组装领域的研究仍较少，尤其是涉及具有刺激响应性的嵌段/无规共聚物的研究更是鲜有报道。本文采用 RAFT 聚合方法合成了一系列的 POSS 基双亲嵌段/无规共聚物，我们对其在水溶液中的自组装行为进行观察，并深入研究了自组装纳米粒子的刺激响应性。本论文的主要工作具体如下：

1. 嵌段共聚物 PMAPOSS-b-P(NIPAM-co-OEGMA)的合成、表征和温度敏感性。采用 RAFT 聚合法成功合成了 PMAPOSS-b-P(NIPAM-co-OEGMA)嵌段共聚物，通过 NMR、FTIR、GPC、和 TGA 等表征方法对产物的结构和热性能进行了表征。利用嵌段共聚物的两亲性在水溶液中制备了自组装胶束，并采用荧光光谱法、DLS、TEM 和 UV-vis 等表征方法对制备的共聚物自组装形貌、胶束临界胶束浓度（CMC）和温度响应性等进行了表征。着重探索了胶束溶液的温度敏感性，我们发现这种新型有机-无机杂化嵌段共聚物溶液在升温时会经历一个由四个阶段组成的相变过程，最终形成胶束团簇。我们系统研究了嵌段共聚物的结构、分子量及溶液浓度对温度敏感性的影响。此外我们还对这种嵌段共聚物温度敏感性的可逆性进行了研究，发现溶液浓度对此嵌段共聚物温敏性的可逆性程度具有非常大的影响。

2. 无规共聚物 Poly(MAPOSS-co-NIPAM-co-OEGMA-co-2VP)的合成、表征和多重刺激响应性。采用 RAFT 聚合法成功合成了无规共聚物 Poly(MAPOSS-co-NIPAM-co-OEGMA-co-2VP)，通过 NMR、FTIR 和 GPC 等表征方法对产物的结构进行了表征。利用无规共聚物的两亲性在水溶液中制备了自组装胶束，并采用 DLS、TEM 和 UV-vis 等表征方法对制备的共聚物自组装形貌、尺寸及多重刺激响应性进行了表征。共聚物在水中能够自组装成球型胶束，胶束尺寸随着 pH 的下降，会经历先增大后减小的过程。溶液中多价金属盐的浓度对

共聚物胶束的稳定性有很大影响。我们发现存在一个临界金属离子浓度 CCC，当溶液中多价金属离子的浓度超过 CCC，共聚物胶束会通过吡啶基团与金属离子的配位作用形成球型的胶束团簇络合物。DLS 和 UV-vis 结果表明，这种新型无规共聚物具有灵敏的最低临界互溶温度 LCST。我们系统研究了无规共聚物的结构、分子量、溶液浓度以及 pH 对 LCST 的影响。最后我们还对这种无规共聚物温度敏感性的可逆性进行了研究，发现溶液浓度对其温敏性的可逆性程度具有非常大的影响。

3. 无规共聚物混合胶束的制备及静电作用对温度敏感性的影响。采用 RAFT 聚合法成功合成了无规共聚物 Poly(MAPOSS-co-NIPAM-co-OEGMA-co-AA)，通过 NMR、FTIR 和 GPC 等表征方法对产物的结构进行了表征，并通过 DLS 和 TEM 对制备的共聚物的自组装形貌尺寸进行表征。利用 Poly(MAPOSS-co-NIPAM-co-OEGMA-co-2VP)无规共聚物的胶束同 Poly(MAPOSS-co-NIPAM-co-OEGMA-co-AA)无规共聚物胶束进行共混制备混合胶束，并采用 DLS、TEM 和 UV-vis 等表征方法对制备的共聚物混合胶束的形貌、尺寸及温度敏感性等进行了表征。研究发现不同 pH 下所形成的混合胶束尺寸不同，而且在 pH 7.0 时，混合胶束具有最大的尺寸。我们将其归结于不同 pH 下的混合胶束静电作用力大小的不同。另外，探索了不同 pH 下混合胶束溶液的温度敏感性，在 pH 7.0 的水溶液的所得的混合胶束具有最大的 LCST，且其值远大于其他 pH 下混合胶束的 LCST。对于不同 pH 下所形成的混合胶束 LCST 的不同，我们同样将其归结于不同 pH 下的混合胶束静电作用力大小的不同。此外，我们发现混合胶束的 LCST 对其组成具有巨大的依赖性，随着 2VP（40）胶束含量的提高而增大，随着 AA（40）胶束含量的提高而减小。除此之外，我们发现所得到的混合胶束的温度敏感性行为具有完全可逆性。

关键词：POSS；嵌段/无规共聚物；自组装；刺激响应性

Abstract

Recently, organic/inorganic material serves as novel hybrid composites, which possess the virtues of organic polymers and inorganic materials, has been attracting significant attention. The emergence of POSS, which has nature nanoscale, neat space structure, designature molecular structure and good solubility, provides a new way for the application and development of organic/inorganic hybrid materials. Meanwhile, it makes it possible to modify polymers from the real single nanoscale and molecular level. However, little attention has been focused on the synthesis and self-assembly behaviors of block/random copolymers containing POSS with novel architectures, especially these hybrid assembles that can respond to multiple external stimuli. Herein, we successfully synthesized some hybrid block/random copolymers containing POSS via RAFT polymerization. The self-assembly behaviors and stimuli-responsive property have been examined in depth.The main achievements of this work were shown as follows:

1. Synthesis, characterization, and temperature responsive behaviors of a novel block copolymer containing POSS. In this part, the synthesis of PMAPOSS-b-P (NIPAM-co-OEGMA) block copolymers via RAFT polymerization was investigated seriously. Furthermore, the structure and thermal properties of these products were characterized by NMR, FTIR, GPC, and TGA. We prepared the micelles of PMAPOSS-b-P(NIPAM-co-OEGMA) in aqueous solution, and carefully investigated the self-assembly morphology, critical micelle concentration (CMC), and temperature responsive behaviors by fluorescent spectrometry, DLS, TEM and UV-vis. We put great interest in the temperature responsive behaviors and the results revealed a four-step phase transition with the copolymer solution heating. When it came to the fourth step, the original micelles would aggregate to arise micelle clusters. Some factors such as the concentration, molecular weight and copolymer generation that may affect the cloud point were studied systematically. In addition, these novel hybrid

micelles would undergo an association/disassociation cycle with the heating and cooling of solution, and the degree of reversibility displayed tremendous concentration dependence.

2. Synthesis, characterization, self-assembly behaviors and multiple responsive properties of a novel random copolymer containing POSS. In this part, random copolymers Poly(MAPOSS-co-NIPAM-co-OEGMA-co-2VP) were synthesized via RAFT polymerization, and the structure of these products were characterized by NMR, FTIR and GPC. The self-assembly morphology, micelle size, and multiple stimuli-responsive behaviors of the novel copolymer were investigated by DLS, TEM and UV-vis. The results indicated the novel random copolymer in water could self-assemble into spherical aggregates and the self-aggregate size displayed a remarkable dependence on pH, which would first increase and the then decrease with pH decreasing. The stimuli-responsive characteristics of these assembles were tested by means of UV-vis spectra, DLS and TEM. There was a critic Zn^{2+} concentration over which the aggregates could be coordinated into well-define spherical aggregate clusters. Results from UV-vis and DLS revealed that the copolymer solutions exhibited a sharp and intensive lower critical solution temperature (LCST). Some factors such as the solution concentration, molecular weight, pH and copolymer generation, which could affect the cloud point, were studied systematically. In addition, these novel hybrid aggregates would undergo an association/disassociation cycle with the heating and cooling of solution and the degree of reversibility showed strong concentration dependence.

3. Hybrid micelle self-assembled from interpolyelectrolyte complexation: the effect of electrostatic interaction on temperature responsive behaviors. In this part, random copolymer Poly(MAPOSS-co-NIPAM-co-OEGMA-co-AA) was synthesized via RAFT polymerization, and the structure and self-assembly morphology of these products were characterized by NMR, FTIR, GPC, DLS and TEM. Hybrid micelles were prepared from the chain exchange between Poly(MAPOSS-co-NIPAM-co-OEGMA-co-2VP) micelles and Poly(MAPOSS-co-NIPAM-co-OEGMA-co-AA) micelles. The self-assembly morphology, micelle size, and temperature responsive

behaviors of hybrid micelle were investigated by DLS, TEM and UV-vis. The results indicated hybrid micelle size displayed a remarkable dependence on pH and possessed the largest size at pH 7.0, which may derive from the huge difference in electrostatic interaction at different pH. At the same time, we studied the temperature responsive behaviors of hybrid micelle at different pH. To our surprise, the largest LCST emerged at pH 7.0 and far more than that of other pH. We also attributed the above phenomenon to the difference in electrostatic interaction at different pH. Furthermore, we found the LCST of hybrid micelles was greatly dependent on generation, which increased with 2VP（40）micelle content and decreased with AA（40）micelle. What is more, these novel hybrid micelles would undergo wholly association/disassociation cycle with the heating and cooling of solution.

Keywords: POSS; block/random copolymer; self-assembly behavior; stimuli-responsive property.

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第一章 绪论

1.1 POSS 的简介

1.1.1 POSS 的结构与性能

高分子科学自 20 世纪 30 年代发展以来，在生产和生活等方面给人们带来极大的便利与享受。但是相对金属、陶瓷材料，高分子材料普遍具有较低的模量和强度。一种有效的途径是使用纳米无机粒子来提高高分子的性能，制备有机-无机杂化材料。这种方法不仅能保持高分子材料本身的低密度和强韧性的优点，而且能引入无机材料的良好热稳定性、抗氧化性等优点[1-6]。目前已知的纳米填料有球状的（如金属或半导体纳米粒子）、层状的（如粘土）或者中空的（如纳米纤维和碳纳米管）。这些有机-无机杂化材料具有多重功能性并在电子器件、生物敏感器和催化等方面具有广大的应用前景[7]。

可控结构的无机纳米粒子团簇，尤其是多面体齐聚倍半硅氧烷（Polyhedral oligomeric silsesquioxanes，简称 POSS）的出现为有机/无机纳米杂化材料应用和发展提供了一种新的途径。作为一类本身含有无机/有机混合结构的杂化纳米化学填料，多面体齐聚倍半硅氧烷将“有机-无机纳米复合”之一概念推进到近乎完美，将其引入到聚合物中可提高热性能、力学性能，降低其介电常数、表面能等。倍半硅氧烷(silsesquioxone)是一类具有化学结构式为$(RSiO_{1.5})_n$ 的化合物，其中 n=6、8、10、12，R 可以是 H 或者烃基、烯烃、芳基、芳烯基以及它们的有机衍生物[8]。其结构包括无定形结构、梯形结构、笼状结构、半笼结构，如图 1.1 所示。POSS 是倍半硅氧烷的一种，它包括无机和有机两个部分，硅和氧构成无机内部结构，极性或非极性的有机成分构成外部结构。POSS 纳米粒子的直径从 1 nm 到 3 nm，另外 POSS 分子外部结构所含有的有机基团，可以使 POSS 纳米结构与聚合物、生物系统表面有很好的相容性。下面结合 POSS 特殊的结构来阐述其独特的优越性。

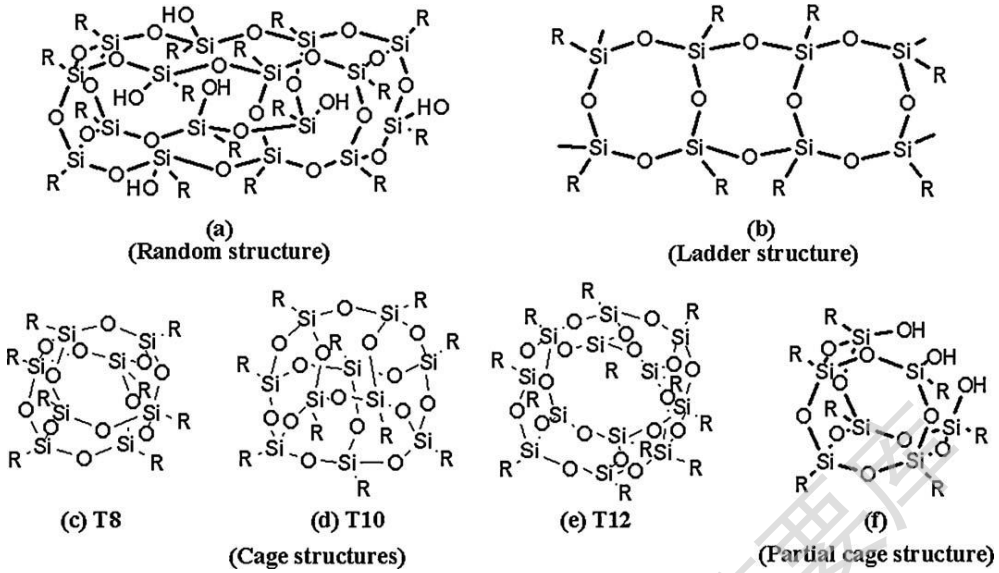

图 1.1 倍半硅氧烷的结构

Figure 1.1 The structures of silsesquioxone

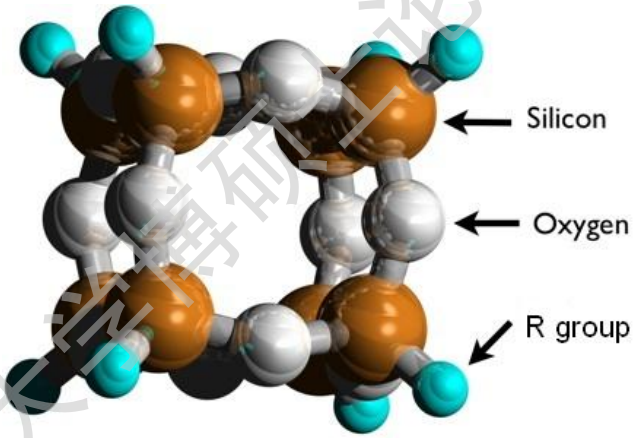

图 1.2 多面体低聚倍半硅氧烷的结构示意图

Figure 1.2 Structure of Polyhedral Oligomeric Silsesquioxanes

（1）分子内杂化结构。典型的 POSS 分子如图 1.2 所示，核心是硅氧组成的笼形无机骨架，顶点 Si 连接有机基团 R，其本身就是一个分子水平上的有机/无机分子内杂化体系。这种结构不仅综合了有机和无机组分各自的优越性，而且还能由于二者的协同效应产生新的性能[9-10]。

（2）纳米尺寸效应。POSS 本身是一种具有纳米尺寸的化合物，三维尺寸为 1～3nm，是最小硅颗粒，其物理尺寸与大多数聚合物链段在同一数量级。独有的六面体结构具备小尺寸效应、表面界面效应、量子尺寸效应、宏观量子隧道效应，